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ANNUAL REPORT

October 1, 1979- September 30, 1980

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

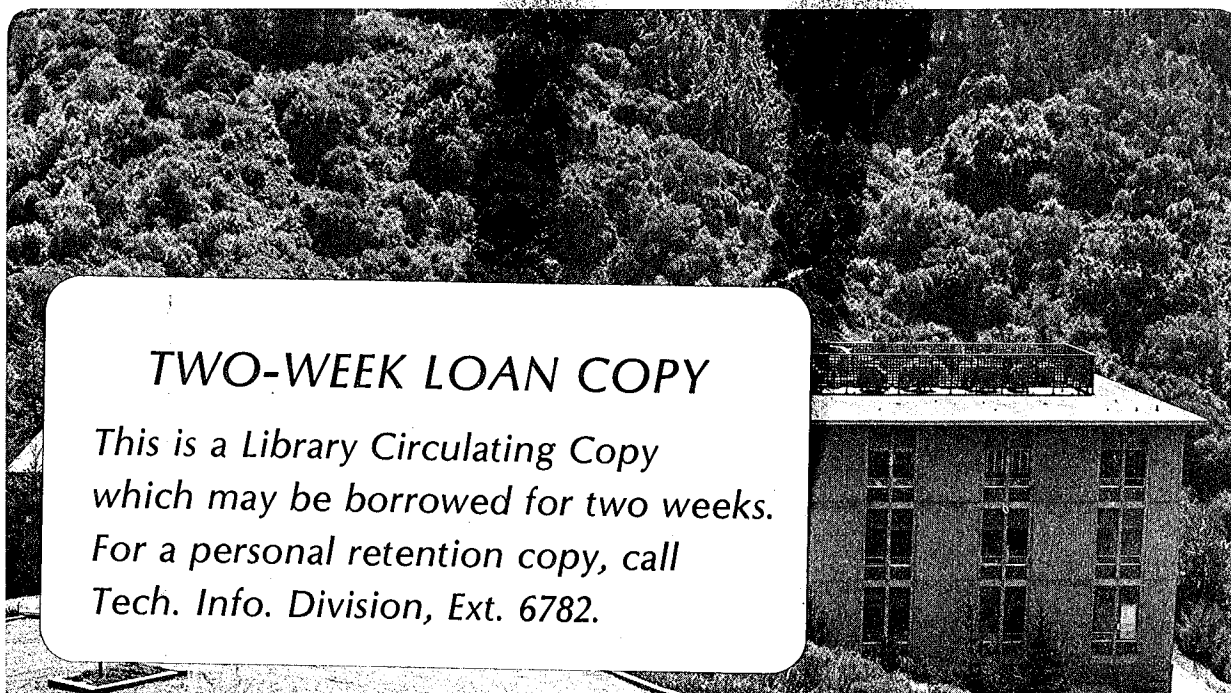
Heinz Heinemann

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ANNUAL REPORT

October 1, 1979 - September 30, 1980

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

Contract ET-78-G-01-3425

Principal Investigator: Heinz Heinemann

Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720

This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy, Chemical Sciences Division and the Assistant Secretary of Fossil Energy, Office of Liquefaction, Advance Research, Fossil Fuels Division of the U.S. Department of Energy under Contract W-7405-ENG-48.

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Introduction

Quarterly reports on progress of this contract have been issued in December, 1979, and March and June 1980. The present annual report summarizes these quarterly reports and includes work performed during the last quarter of fiscal 1980. The reviews of the six different tasks have been written by the Task Managers.

The first year of this project has just been completed and much of the time and effort has been concentrated on equipment building, assembling, testing, and on staffing. This, of course, has been more true in the areas of work with spectroscopic and high pressure equipment than in organic chemical reactions. More experimental results are therefore reported in the areas of hydrogen transfer mechanisms and catalysis and organo-metallic chemistry.

A few of the significant results in these and other areas are the evidence for catalysis in hydrogen transfer from tetralin; a novel and possibly very important new synthesis of alkyl aromatics from benzene, carbon monoxide, and hydrogen; the study of coals in the transmission electron microscope identifying coal macerals, minerals and metals, and leading to the possibility of observing location of and catalytic influences on pyrolysis and hydrogenation at elevated temperatures; the finding that scales formed on deactivated cobalt-molybdena-alumina-hydrogenation catalysts contain not only metals from the liquid feedstocks, but also molybdenum sulfide which must derive from migration from the catalyst interior to and beyond the surface.

Substantial experimental progress can now be expected in each quarter of the second year. Insights gained in mechanisms of pyrolysis, hydrogenation, hydrogen transfer, and indirect liquefaction of coal promise to lead to improving technology by defining problem areas and showing routes to by-pass problems.

B

This project has brought together a team of organic, physical, and organometallic chemists, of chemical engineers and of material scientists, some of whom have had extensive industrial experience. In regular meetings, the advantages of an interdisciplinary approach have become apparent in the numerous discussions and suggestions, often coming from analogies in other areas. Finally, the project provides an excellent training ground for future workers in synthetic fuels research and development, since all work is carried out by graduate students and post-docs under the leadership of experts in a variety of fields.

Selective Synthesis of Gasoline Range Components from CO and H₂

Task Manager: A. T. Bell

The problem with conventional Fischer-Tropsch synthesis is that it produces a very broad spectrum of products which requires substantial separation and refining to produce gasoline. It has been suggested that the character of the product distribution is a result of the chain growth mechanism, which is envisioned to involve a stepwise addition of monomer units (i.e., -CH₂-). Such a process leads to a product distribution characterized by Schultz-Flory kinetics. Following this line of reasoning, it is concluded that there is a limit to the maximum yield of a given product. Thus, for example, the maximum yield of gasoline range components (C₅-C₁₁) is calculated to be 48%. To surpass this figure, catalyst systems must be found that are not constrained by the polymerization kinetics or that limit chain growth by the design and size of the catalyst pores. The objective of this program is to establish how modifications in catalyst composition and reaction conditions might be used to produce gasoline range components with selectivities surpassing those attained by conventional Fischer-Tropsch synthesis.

Two approaches to altering product distribution will be explored. The first involves the use of small pore diameter zeolites as supports for Fischer-Tropsch catalysts. Published studies suggest that by using such supports the formation of very high molecular weight products can be eliminated. The second approach involves the examination of whether olefins, which are produced as primary products of Fischer-Tropsch synthesis, can be used to suppress the formation of methane and high molecular weight products. The objective here is to use olefins as scavengers for intermediates containing single carbon atoms (e.g., methylene groups), which contribute to both methanation and chain growth.

Research Accomplishments

The design and construction of the experimental apparatus have occupied a major portion of the time during the past year. Two catalyst testing units were designed and constructed. The first utilizes a fixed bed of catalyst and is intended for screening of new catalyst preparations. The second unit uses a high pressure stirred autoclave. This reactor can be used to study mass transfer effects with either catalysts in oil suspensions or larger catalyst particles contained in a rotating basket.

A schematic of the apparatus used in conjunction with the autoclave reactor is shown in Fig. 1. Reactants are purified and then fed to the autoclave via mass flow controllers. The use of such controllers makes it possible to maintain a constant supply of H₂ and CO over long durations. The reactor is a 450 cm³ Parr autoclave. This unit is fitted with a thermocouple well and an impeller which can be rotated at speeds of up to 1000 rpm. The autoclave can be maintained at elevated temperatures by means of a furnace connected to a temperature controller.

Both the gases effluent from the autoclave and the liquid contained within it are analyzed by gas chromatography. The gaseous products are sampled from a heat-traced line maintained at reaction pressure. The hydrocarbons present in the gas phase are analyzed on a 50 m glass

capillary column coated with OV-101 and contained within a Varian Aerograph Model 3700 gas chromatograph. The products leaving the capillary are detected by a flame ionization detector. The contents of CO, H₂, and C₁ through C₅ hydrocarbons in the product gas are analyzed using a 3 in column packed with Chromsorb 106. The effluents from this column are detected by a thermal conductivity detector. An analysis of the liquid in the autoclave is achieved using the capillary column. The data generated by the chromatograph are stored on-line using a Commodore PET microprocessor connected to a floppy disc. Following acquisition, the data are analyzed to determine peak areas and a table of product composition is generated by the microprocessor. It is anticipated that by using such a sophisticated product analysis scheme it will be possible to obtain a complete mass balance around the reactor.

The flow manifold used in conjunction with the fixed bed reactor is similar to that shown in Fig. 1. The reactor in this case is a stainless-steel tube which is heated in a temperature-regulated sand bath. The gaseous reaction products from this reactor are analyzed using the procedures described above. Thus, the chromatograph and data acquisition system serve both reactor systems.

Future Research Plans

With completion of the experimental apparatus, efforts will begin to meet the stated research objectives. It is proposed to investigate first the performance of alumina-supported iron and ruthenium catalysts with different levels of potassium promotion. Three objectives have been set for these studies. The first will be to establish empirically the influence of conversion on the distribution of organic products formed. Preliminary studies suggest that low molecular weight olefins formed via primary reactions are reincorporated during the latter stages of reaction, thereby suppressing the formation of methane and very high molecular weight products. The implications of these initial results will be examined to determine whether secondary reactions can be used to control significantly the ultimate distribution of hydrocarbons formed. The second objective will be to determine the extent to which the oxygen released during Fischer-Tropsch synthesis can be rejected as CO₂ rather than water. The influence of gas space velocity on the extent of conversion will be examined as well as the effect of potassium loading. Here again, initial studies have shown that the extent of CO₂ formation relative to H₂O increases as an iron catalyst is promoted with potassium. The extent to which a ruthenium catalyst might be similarly affected is little known and worthy of investigation.

Following these experiments experiments will be conducted using iron and ruthenium supported on ZSM-5 and related zeolites. The purpose of this work will be to establish the role of the zeolite in controlling the molecular weight distribution of the products formed. In addition, efforts will be made to establish whether the metallic component substituted into the zeolite is stable or whether the metal migrates to the outer surface of the zeolite particles.

Detailed studies of the effects of mass transport and olefin reincorporation will be conducted using the autoclave apparatus. Several objectives will be pursued. The first will be to establish the extent to which catalysts suspended in an oil phase produce product distributions similar to those obtained in the fixed bed reactor. In this connection

it will be important to establish what, if any, effect liquid phase mass transfer of H_2 and CO have on the product distribution formed. A second objective will be to determine whether the olefins formed via primary reactions can be reincorporated more effectively when the catalyst is an oil suspension than when the catalyst is present in a fixed bed.

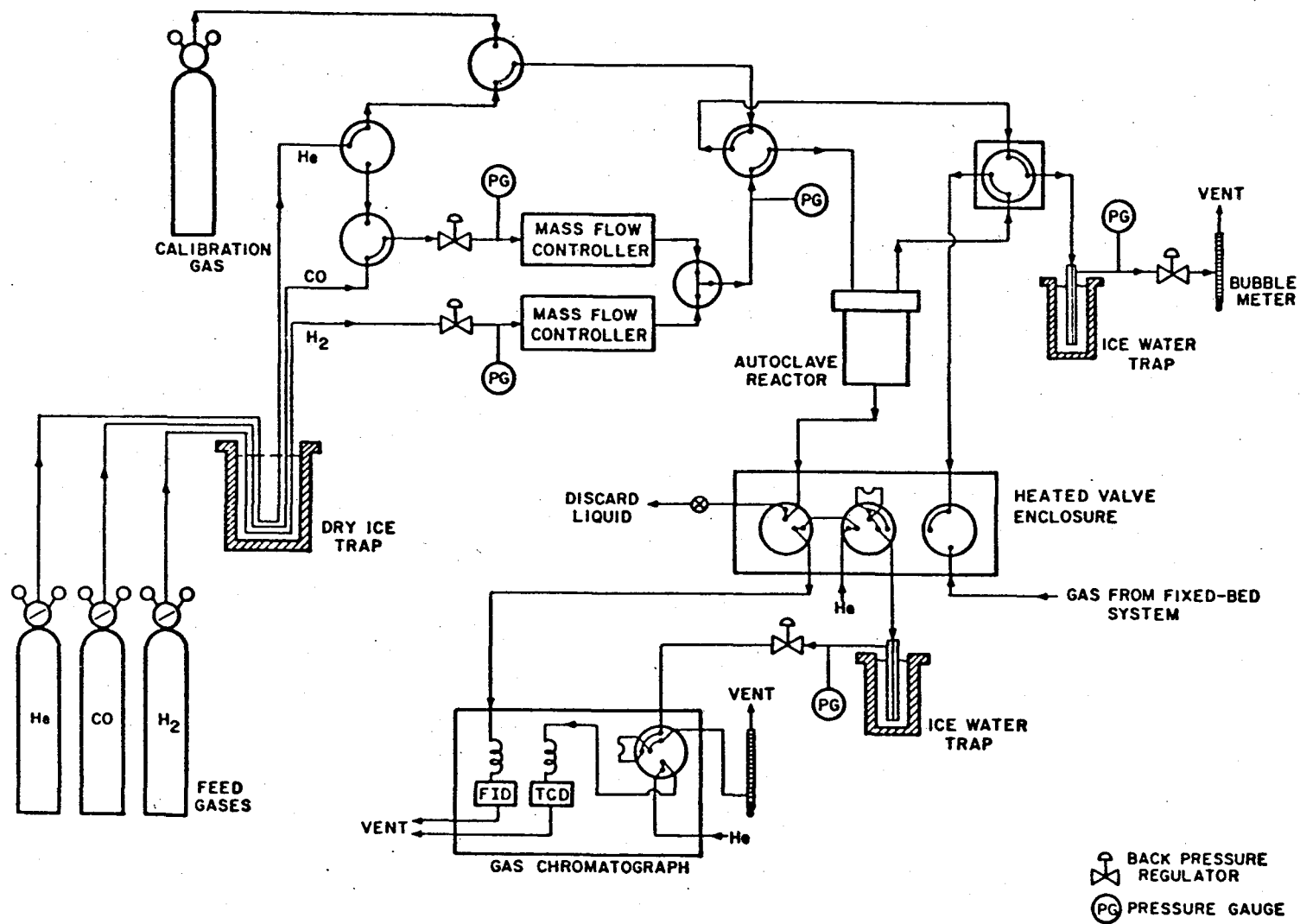


Figure 1.

Electron Microscope Studies of Coal during Hydrogenation

Task Manager: J. W. Evans (with J. A. Little and M. I. Perez)

INTRODUCTION

It has recently been realized that the inherent mineral matter in coal has an effect on its behavior during gasification and liquefaction processes (1) although neither the precise mode of operation of this effect nor the particular minerals involved are well understood. Also both the structure and the maceral content of the coals are obviously important in conversion reactions. This structure is reflected in the size and distribution of the pores in the coal as well as the grain size and shape of the various constituents. These problems suggest microscopic investigations of various coals and thus this project will concentrate on the characterization of coal microstructures and observation of the gasification reactions in-situ in an environmental cell. At this point the study has concentrated on the initial characterization of coal microstructures using a Phillips 400 TEM/STEM microscope but will be broadened to include the use of a small environmental cell in a Hitachi 650 kV microscope so that both the temperature and pressure of different gases can be simultaneously controlled over the specimen whilst it is being viewed directly in electron transmission. A residual gas analyzer has also been purchased from Anacon Ltd. so that the gases leaving the environmental cell can be monitored and the course of the conversion reaction can be followed kinetically.

EXPERIMENTAL

The inhomogeneity and reactivity of coal means that great care must be taken in preparing representative specimens for the microscope. The procedure adopted involves very careful hand grinding and polishing on successive

diamond pastes down to a 0.25 μm paste, until the specimens become optically transparent. At this stage specimens are approximately 5-10 μm thick and as ion-thinning machines thin at approximately 2 $\mu\text{m}/\text{hour}$ then a mere 2-3 hours are required for final thinning.

RESULTS AND DISCUSSION

Figure 1 shows a high-ash anthracite which was found to contain many particles which contained only titanium as seen in the X-ray display (Fig. 1, at A). By using a finely focussed electron beam with a probe diameter of approximately 100A, micro-micro diffraction patterns could be obtained and the mineral particle identified as anatase, a form of TiO_2 . The detection of titanium bearing particles is important as titanium has a detrimental effect on the Co-Mo catalyst used in liquefaction processes. Figure 1 (B and C) shows a large grain of clay, the extensive streaking of the diffraction spots indicating that the grain is composed of very many thin clay platelets. Although the mineral underwent rapid degradation under the electron beam (eg. at C), it was tentatively labelled as sericite, a form of muscovite.

Figure 2 shows a montage of micrographs indicating the sequence of events from identification of the macerals in a high volatile class A bituminous coal by optical methods, to examination in the electron microscope. Figure 3 shows micrographs of the two different areas 'A' and 'C' shown in Figure 2. Figure 3a is from a fusinite band and shows particles tentatively identified as kaolinite from the X-ray and diffraction data. Figure 3b is from the vitrinite region of the specimen (C) and 3c shows an electron micrograph from the Telocollinite region with very small regularly shaped particles containing mainly aluminum with a small amount of calcium.

Figure 4 shows an example of a Western sub-bituminous coal. The high moisture content of this coal together with its high volatile content may make it susceptible to partial charring in the ion-beam thinner. The catalytic effect of certain minerals within coals is often ascribed to their ability to 'wet' the surface of the coal and provide additional reaction sites (2). As a possible semi-char this coal will already have "gasified" to some extent and therefore it is instructive to compare the elemental distribution in the coal. This is seen in Fig. 4. Elemental mapping of the silicon and titanium expose the silica and titania particles which appear as essentially discrete particles against a background of random 'noise' from the X-ray detector. The sulphur scan shows a general level of sulphur throughout the sample as might be expected from the organic sulphur in the coal grains, but the calcium scan shows no localization of calcium containing particles but instead a high level of calcium spread evenly over the coal grains of this particular area. Thus it would appear that calcium does have a good ability to 'wet' the surface of the coal.

References

1. Gray, D., Fuel (1978), 57, p. 213.
2. Otto, K., Bartosiesicz, L. and Shelef, M., Fuel (1979), 58, p. 565.

FIGURE 1 Transmission electron micrograph of high-ash anthracite showing a titanium bearing particle at A and a partially degraded clay particle (B and C).

FIGURE 2 Montage of optical and electron micrographs showing the preparation method used to accurately characterize the coals and correlate both optical and electron-optical micrographs. a) Optical micrograph showing vitrinite (c) and fusinite (A) bands. b) The same areas as a) mounted in a folding grid. c) The same area as a) and b) viewed in transmitted light. d) The area after ion beam thinning. e) Low magnification electron micrograph of the sample. f) Higher magnification electron micrograph showing more image detail.

FIGURE 3 Electron micrographs showing microstructures and particles associated with the different macerals in the coal. a) Particles of Kaolinite in the fusinite band. b) Microstructure of the vitrinite band. c) Microstructure and particles from a tellocollinite region.

FIGURE 4 Elemental distribution in the sub-bituminous coal specimen. a) STEM micrograph of area. b) X-ray analysis of the whole area. c) Silicon map. d) Titanium map. e) Sulphur map. f) Calcium map.

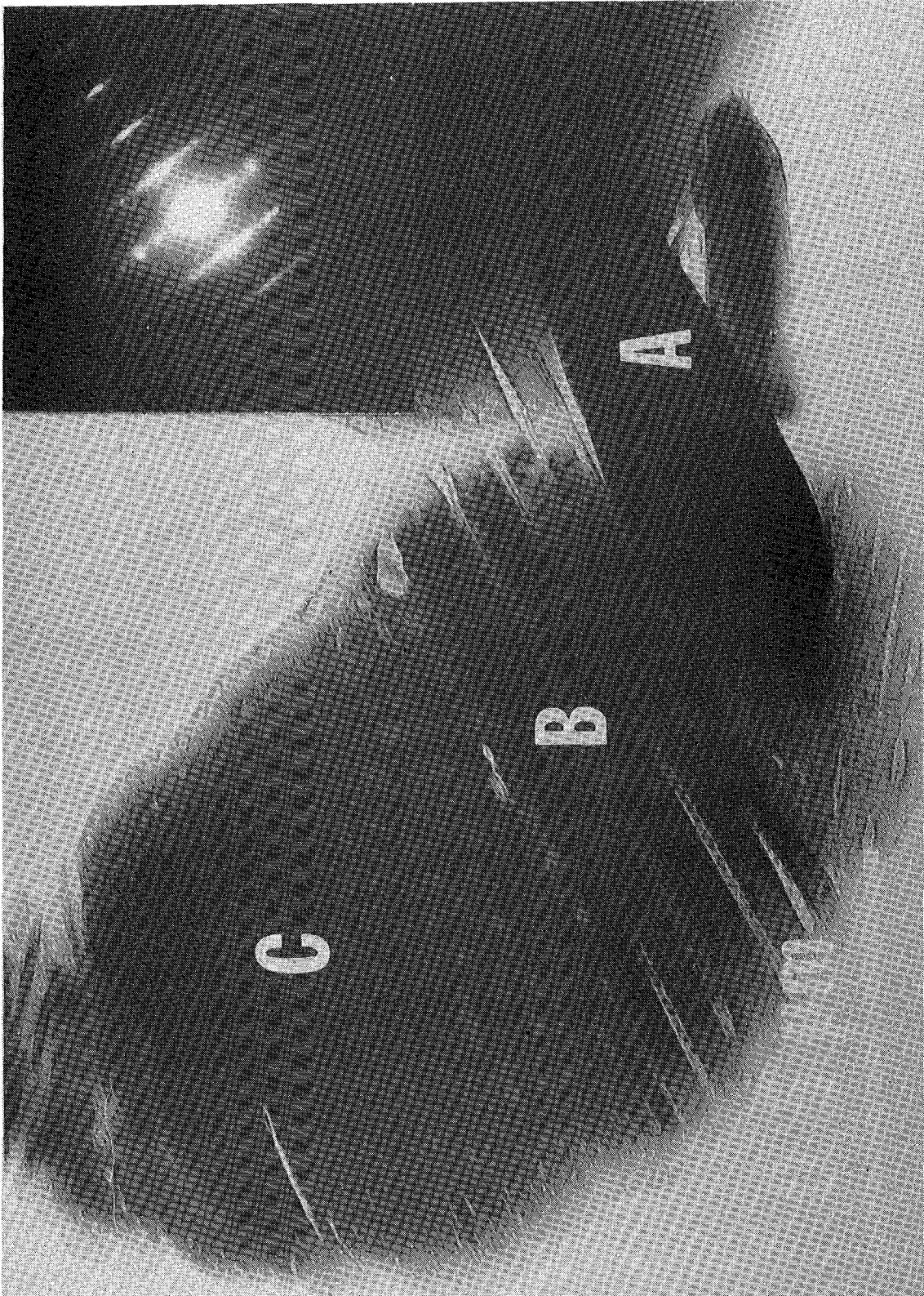


Figure 1

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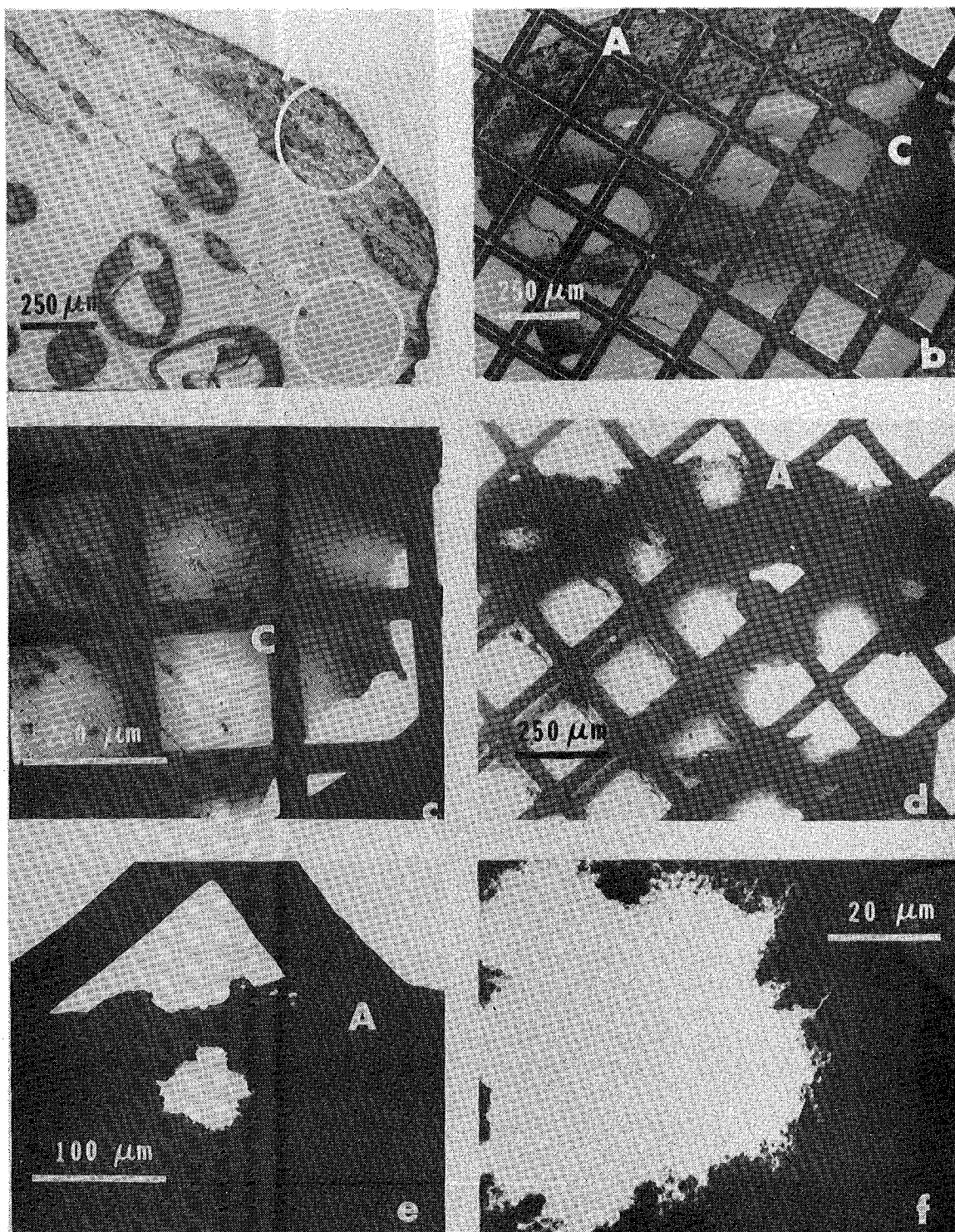


Figure 2

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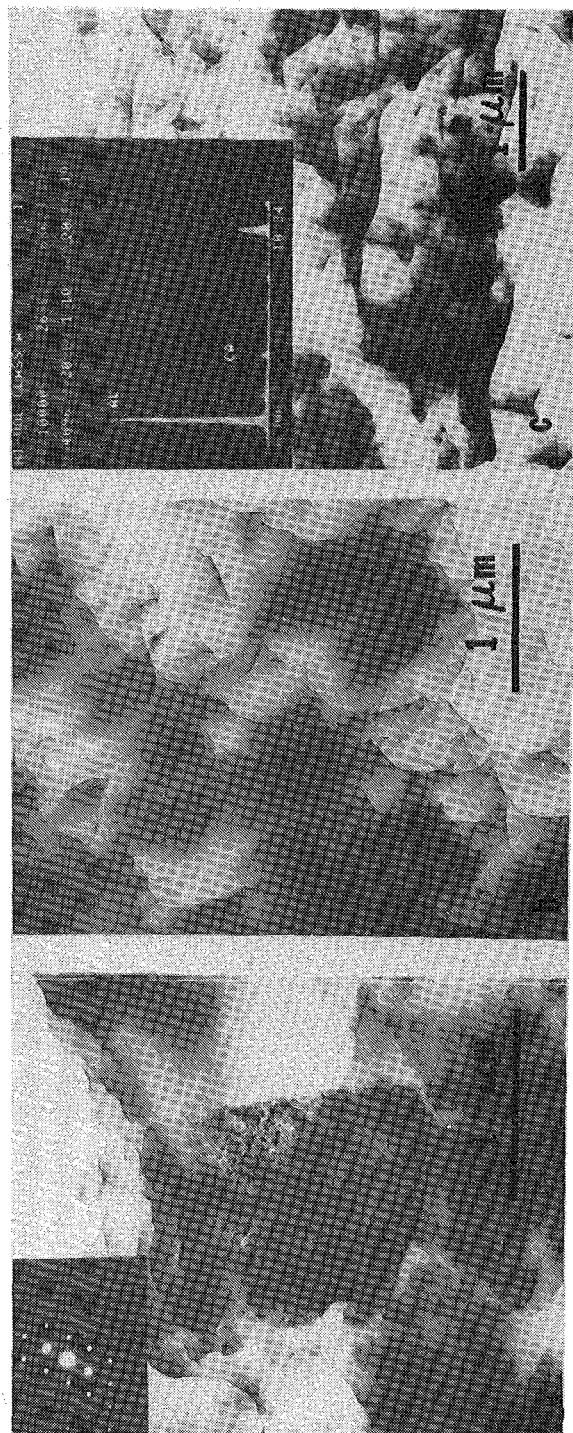


Figure 3

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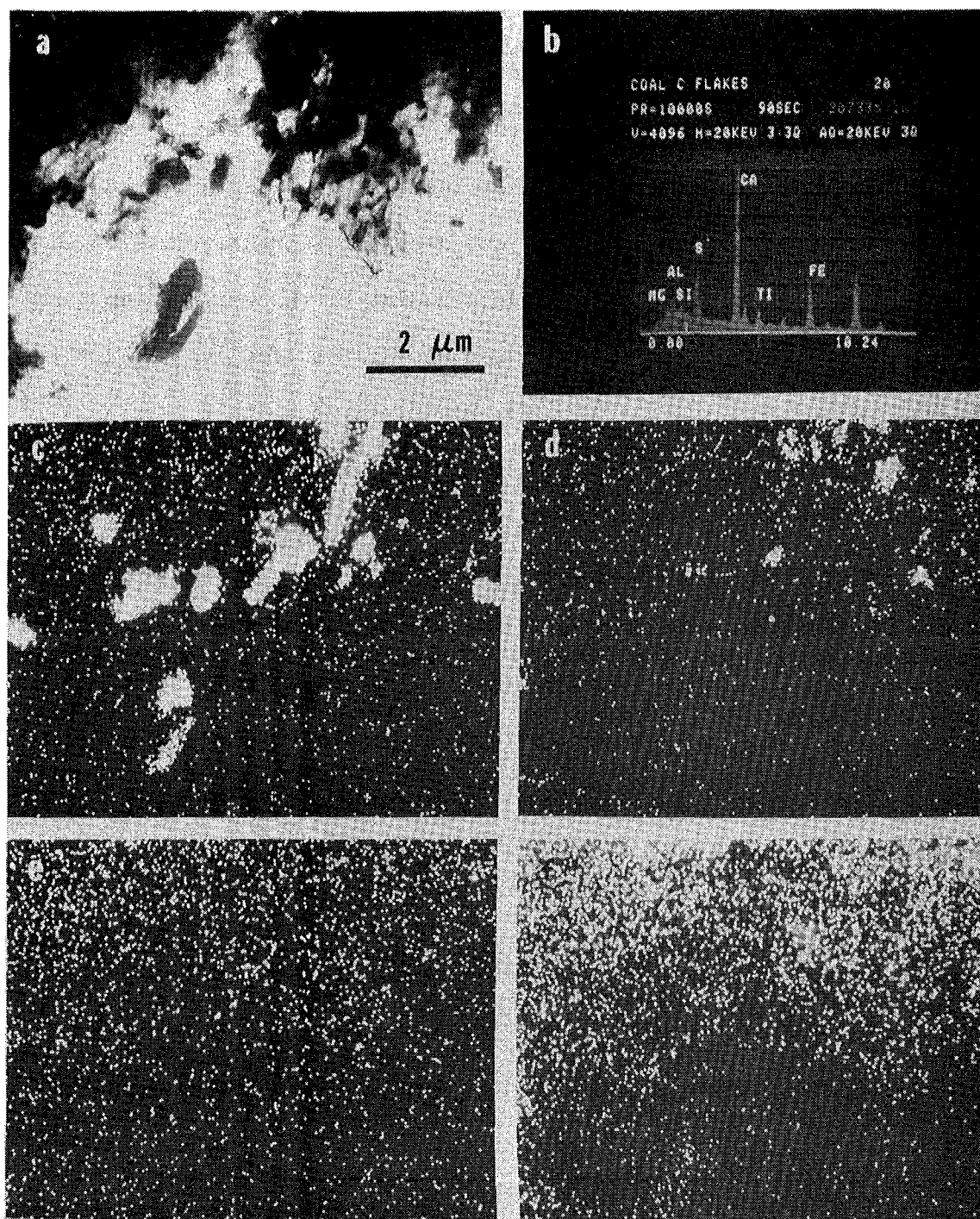


Figure 4

XBB 807-8747

TASK 3: Catalyzed Low Temperature Hydrogenation of Coal

Task Manager: G. A. Somorjai
Work with A. Cabrera

The purpose of our studies is to develop catalysts that will aid the hydrogenation and hydrogenolysis of coal at low temperatures (below 500°C). In this way we hope to obtain a large yield of hydrocarbons directly from coal instead of gasification to CO and H₂. Since Bergius¹ in 1911 initiated research in direct hydrogenation of coal, this subject has been intensively studied by various researchers. Nevertheless, an understanding of the reaction mechanism as well as the role of catalysts used has not as yet been achieved. With the advancement of surface analysis techniques, it is now possible to characterize the structure, composition, and oxidation states of surface atoms and molecules on the atomic scale. Progress made in this field encouraged once again the study of catalyzed coal conversion for the purpose of gathering more information on the basic steps of the process.

There are several recent papers²⁻⁵ on the hydrogenation and oxidation of graphite catalyzed by metal particles (transition metals and alloys of transition metals). Surface characterization in these studies was with electro-microscopy. Instrumentation developed by surface science is capable of combining both studies of the actual kinetics at high pressures and studies of surface analysis in ultrahigh vacuum with the sample *in situ*. We have developed and built an ultrahigh vacuum system with the capability of studying catalytic reactions at high pressures and also characterizing the surface by several techniques in the same chamber. We are presently applying the system to the studies of the catalyzed, low temperature hydrogenation of graphite.

Description of the high pressure system.

This machine is shown in Figure 1. It consists of an ultrahigh vacuum

chamber with a high pressure isolation cell built into it. It is an improved version of an earlier device already reported.⁶ The ultrahigh vacuum chamber has a cylindrical shape with a 12 in. diameter. The UHV is provided by a Varian 1200 liter/sec diffusion pump and a water cooled titanium sublimation pump. This combination can produce a vacuum of better than 10^{-10} Torr. The sample is placed in the center of the axis of the chamber and it is accessible to low energy electron diffraction, Auger electron spectroscopy, and photoelectron spectroscopy techniques of analysis, ion bombardment, and mass spectrometer facilities for cleaning and for determination of the surface structure, composition, and oxidation states. When the sample is rotated 180° it allows one to clean the surface on both sides and to perform surface analysis with the techniques mentioned above. The sample may then be enclosed by a small-volume, high-pressure cell which is operated by hydraulic pressure from below. The hydraulic piston applies a pressure of up to 2000 lb/in.² to the cell in order to seal it with a copper gasket. The cell is externally connected to a circulation pump, a pressure gauge, a gas manifold, and a gas sampling valve which is attached to a gas chromatograph.

In the high pressure mode, the isolation cell is closed, the different reactants are admitted in the reaction loop and the circulation pump aids their uniform distribution. The products of the reaction are sampled and analyzed by means of a gas chromatograph. The sample can be heated to a desired temperature by means of electric current; this temperature is monitored with a thermocouple spot-welded to it. A more detailed description of the system is found in Ref.6.

This machine is equipped with low energy electron diffraction optics and a cylindrical mirror analyzer (CMA) mounted on bellows which allow these instruments to move back and forth towards the sample. The optimum performance of the CMA is when the end of the analyzer is at the distance of 0.4 inches from

the sample, and since the diameter of the cell is larger than 0.8 inches, the CMA would be in the way of the cell to be closed. Thus the bellows allows the analyzer to get very close to the sample when the cell is open and to be retracted when the cell is closed. We intend to study the catalytic effects of transition metals evaporated over highly oriented graphite and the catalytic effects of potassium carbonate (K_2CO_3). The plan is to obtain a better characterization of the surface, both the graphite and the deposited catalyst, before studying its interaction with hydrogen, water, oxygen, and carbon monoxide. Then the surface will be characterized again after the reaction. Next we plan to add promoters to the catalysts to study their role in these interactions.

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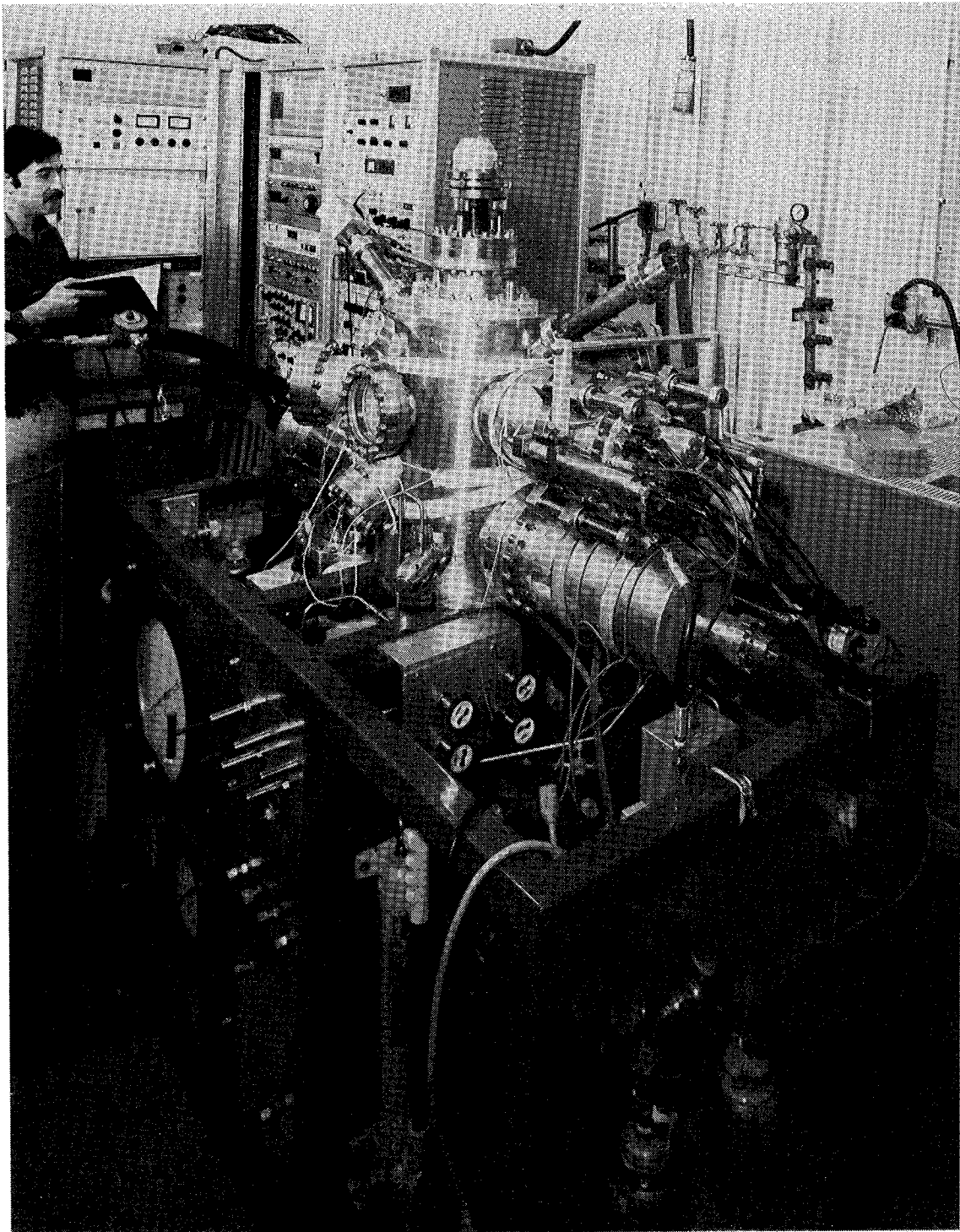


Figure 1

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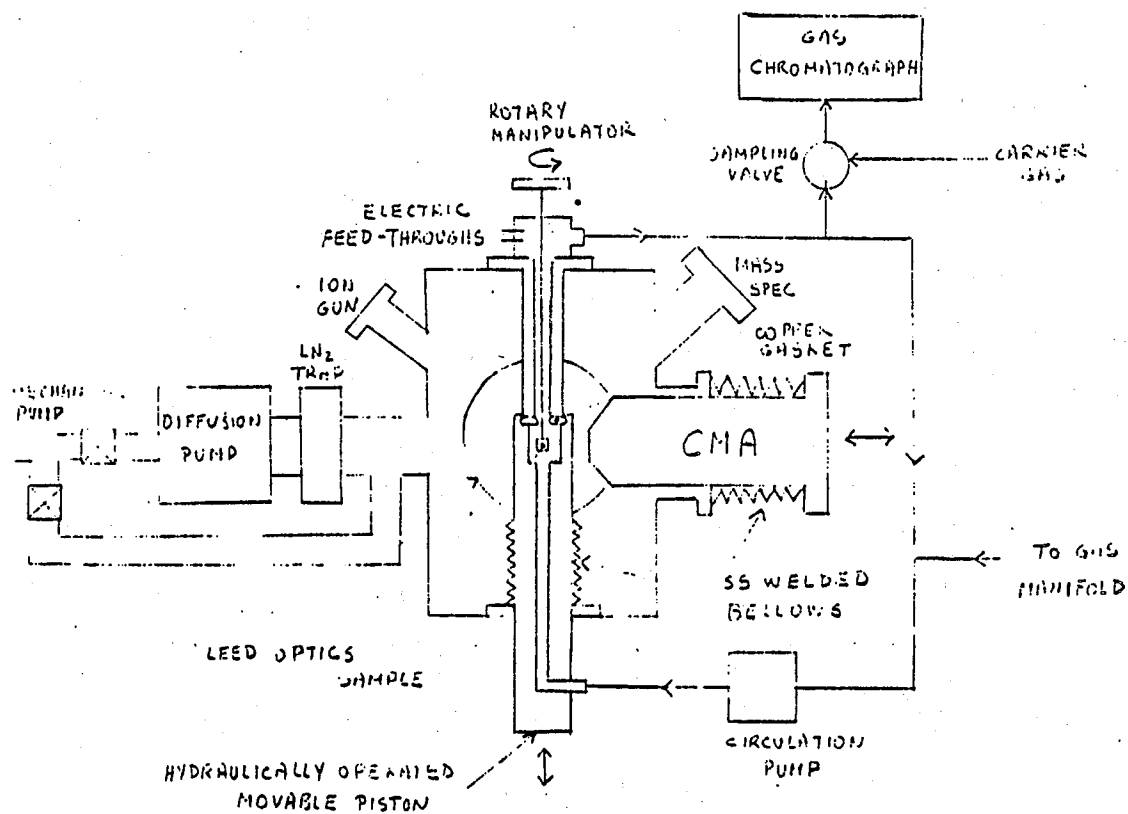


Fig.1 Surface analysis apparatus for catalytic studies at low and high pressures

Figure 1 Diagram

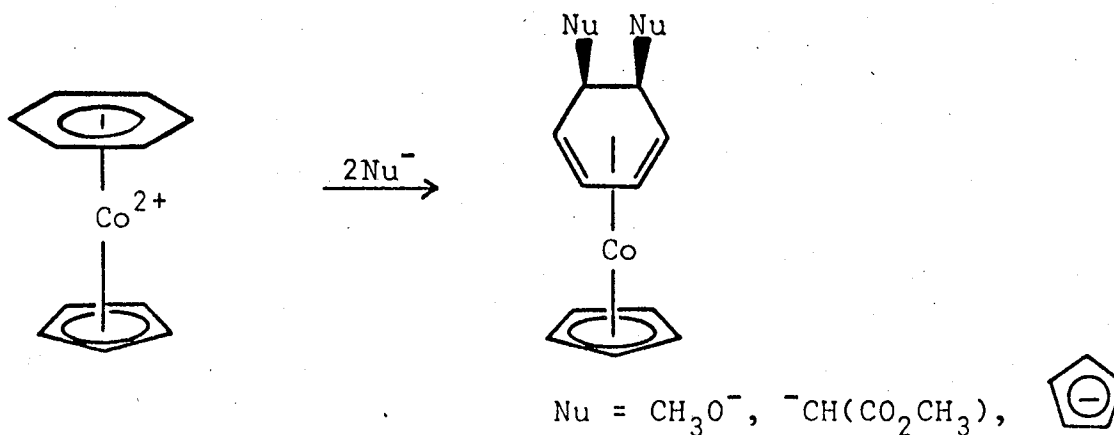
TASK 4

Selective Hydrogenation, Hydrogenolysis, and Alkylation of Coal and Coal Derived Liquids by Organometallic Systems

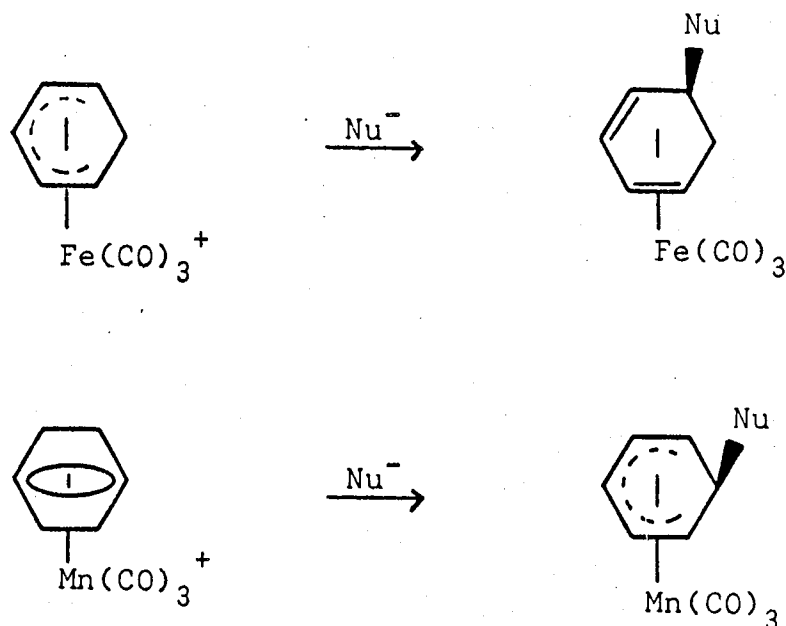
Task Manager: K.P.C. Vollhardt

1. Nucleophilic Additions to CpCo Benzene Dication

In an effort to delineate the potential of using organometallic catalysts and reagents for the nucleophilic depolymerization and lipophilization of coal we have studied model double nucleophilic additions to $\text{CpCoC}_6\text{H}_6^{2+}$. Such additions had been attempted previously by others in rhodium and iridium compounds but had led to only single adducts. We have found that nucleophiles of moderate basicity, e.g. methoxide, malonate, and cyclopentadienide anion, furnish disubstituted complexed cyclohexadienes. Addition occurs vicinally, stereospecifically exo, and to the benzene ring only, in accord with theoretical expectations. Unfortunately, other nucleophiles lead to ligand displacements



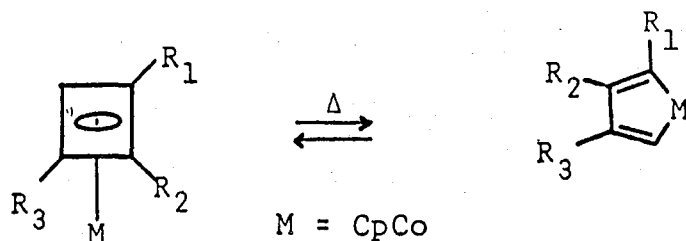
and decomposition. Moreover, the bisadducts are exceedingly thermally and air sensitive precluding further chemistry. Nevertheless, the basic feasibility of this approach to benzene ring substitution has been demonstrated. Several other systems were investigated, particularly complexes based on iron and manganese. New compounds have been fully characterized and analyzed, and the



results obtained will be submitted for publication in due course.

2. Transition Metal Activation of $\text{Csp}^2\text{-Csp}^2$ Bonds

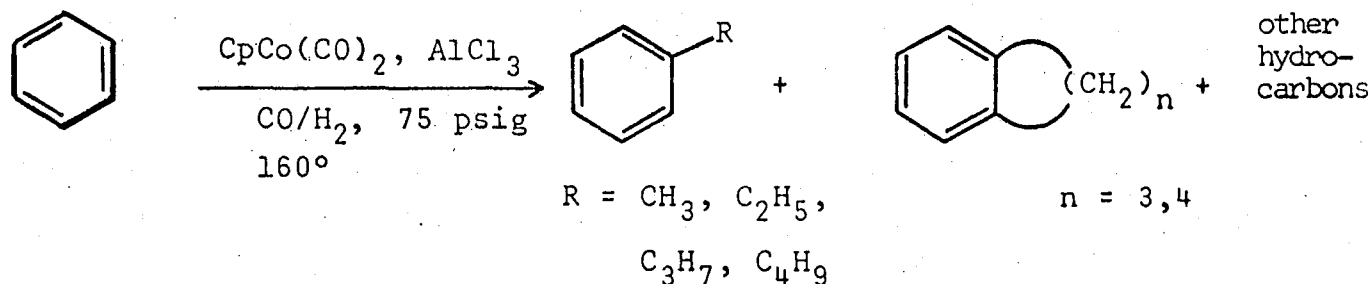
We have for the first time proven the reversibility of an organometallic activation process which is of significance in its potential as a novel method to coal liquefaction by aromatic ring cleavage. This step is an insertion of a transition metal into an $\text{sp}^2\text{-sp}^2$ carbon-carbon bond. This



very basic organometallic step has been demonstrated by the observation of the unimolecular diastereoisomerization of racemic and enantiomerically enriched cyclobutadiene cobalt complexes. If applicable to benzene derivatives, this could become an important activation step for the ring opening depolymerization of coal. In addition, this reaction could potentially be applied to the further functionalization of aromatic molecules with coal-related structures (for example, addition of ethylene, alkynes, carbon monoxide, etc.).

3. Fischer-Tropsch Alkylation of Benzene

In a recent breakthrough a truly remarkable reaction has been discovered. An apparently homogeneous cobalt catalyst, $\text{CpCo}(\text{CO})_2$, will, in the presence of Lewis acids, catalyze the apparent Fischer-Tropsch alkylation of benzene. Mechanistic details and scope and limitations of this reaction are under intensive investigation.



TASK 5

Chemistry of Coal Solubilization and Liquefaction Pyrolysis Studies

Task Manager: R. G. Bergman

a) The Thermal Chemistry of Tetralin

Investigators: Paul B. Comita and Robert G. Bergman

The thermal chemistry of tetralin (1) has been under intense investigation recently¹, due to interest in the fate of hydrogen donors which are used as recycle liquids in the solvent refining of coal. The reactivity of tetralin appears to be dependent on the presence of hydrogen, hydrogen acceptor molecules, different types of reactor surfaces, and surface history. This has resulted in conflicting data in the literature and confusion as to what the thermal reactivity is in the absence of any catalytic effects. In an effort to resolve this situation, we wish to report the reactivity of tetralin resulting from several different methods of activation.

Three methods for energization of 1 were investigated: conventional flow pyrolysis, infrared multiphoton excitation, and sensitized infrared laser thermal activation. All three give rise to six major products: benzocyclobutene (2), styrene (3), o-allyltoluene (4), indene (5), 1,2-dihydronaphthalene (6), and naphthalene (7) (see Scheme 1), and several minor products. The primary concern of this work is to delineate the energetics of the ethylene-loss channel (giving rise to 2 and 3) versus the hydrogen-loss channel (giving rise to 6 and 7) without interference from catalytic effects.

A number of parameters affected the product distribution for the decomposition in a flow reactor, including the composition of the surface, the history of the surface, and the pressure of the system (see Table 1). However, dehydrogenation was always the predominant decomposition mode. Unconditioned surfaces, higher pressures, and longer contact times in the reactor led to more dehydrogenation of 1.

Multiphoton excitation of 1 in the gas phase was accomplished with a pulsed CO₂ TEA laser tuned to 945.99 cm⁻¹. All six major products found from the pyrolysis also resulted from photolysis of tetralin, including one additional product, phenylacetylene. The distribution of these products, however, was at variance with the distribution from the pyrolysis (see Table 1); the major reaction channel for the multiphoton dissociation of tetralin involved ethylene loss.

In the third method of activation, 1 and varying pressures of SiF₄, an inert sensitizer which absorbs strongly in the infrared, were irradiated with an unfocused, pulsed CO₂ TEA laser tuned to 1027.36 cm⁻¹. Pure tetralin does not decompose under unfocused conditions; thus all chemistry is due to sensitization by SiF₄. All six major products were again found.

The number of pulses and the maximum temperature of SiF₄ both had pronounced effects on the product distribution. The variation in the number of pulses had a number of effects. With increasing number of pulses the percentage of 2 and 6 decreased, and the percentage of 3, 5, and 7 increased. This is consistent with 2 and 6 being primary products, and at least some fraction of 3, 5, and 7 being derived from them. Sensitized photolysis of 2 gave rise to a clean isomerization to 3, the sole product of the reaction (70% conversion). Sensitized photolysis of 6 (20% conversion) gave rise to two major products, 7 (68% of product) and 5 (11%).

Temperature variation was achieved by changing the beam intensity and by varying the sensitizer pressure. Less secondary decomposition took place at lower temperatures, and there was a partitioning between the retro-[2+4] product results entirely from C_2H_4 loss and the dehydrogenation is predominantly a result of 1,2-elimination (see Table 2).

Since thermal 1,2-elimination of hydrogen is unusual, the nature of this reaction is of interest. The surface to volume ratio for the photolysis cell had no effect on the ratio of ethylene-loss/dehydrogenation for the sensitized photolysis. The possibility of a radical chain mechanism for the dehydrogenation was tested for by charging the photolysis cell with 1 Torr of nitric oxide. The only observed effect of nitric oxide was to lower the effective temperature for the photolysis. A decrease in the partial pressure of tetralin from 0.325 Torr to 0.032 Torr also had no effect on the ratio of ethylene-loss to dehydrogenation.

We draw the following conclusions from the above experiments: (1) Some fraction of the dehydrogenation reaction in the flow reactor is surface catalyzed. This leads to an anomalously large amount of 1,2-dihydronaphthalene and naphthalene in the reaction products in these flow pyrolysis studies and very likely in all previous investigations. (2) The lowest energy homogeneous reaction channel for tetralin is the retro-[2+4] channel giving rise to benzocyclobutene. This fact is borne out in both the multiphoton and SiF_4 sensitized experiments where surface chemistry does not appear to be important. (3) The low energy dehydrogenation channel of tetralin is almost exclusively 1,2-dehydrogenation. This process, if concerted, is symmetry forbidden and without precedent as the lowest energy dehydrogenation channel in cyclic olefins. Evidence for a radical pathway by radical scavenging experiments was not found. Bimolecular pathways for this process were also not detectable by changing the partial pressure of 1.

Reference:

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Scheme 1

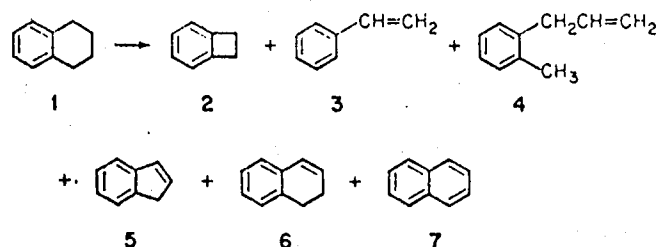


Table I. Product Distribution for Thermal Reaction of 1

conditions	products, %							% conversion of 1
	2	3	4	5	6	7	other	
flow pyrolysis, 1 atm of N ₂ , quartz reactor, 750 °C	2.4 ^{a, b}	18.3	0.5	17.5	10.7	45.8	4.2	74.8
vacuum flash pyrolysis, 0.05 torr, quartz reactor, 750 °C	34.7	9.9	7.9	4.1	31.8	8.2	3.4	3.7
multiphoton excitation, 0.325 torr I, energy/pulse 0.4 J, 13 020 pulses	72.6	11.7 ^c	3.4	4.2	6.2	0.0	2.0	0.5
multiphoton excitation, ^d 0.325 torr I, energy/pulse 0.8 J, 2790 pulses	54.8	19.7 ^c	2.6	5.5	9.0	trace	8.4	0.8
SiF ₄ sensitization, ¹¹ T _{max} 650 °C, 5 torr SiF ₄ , 0.325 torr I, 4960 pulses	58.5	8.3	20.8	2.2	10.3	0.0	0.0	1.5
SiF ₄ sensitization, ¹¹ T _{max} 1490 °C, 6 torr SiF ₄ , 0.325 torr I, 180 pulses	38.2	20.1	8.4	9.4	15.5	5.6	2.8	7.7

^a Numbers are percent of total product found. ^b All data have been corrected for FID response. ^c Includes phenylacetylene response. ^d Visible emission in the focal region was observed in this experiment.

Table II. Deuterium Labeling in Products from Photolysis of 1-d₄^a

product	% of total mixture	isotopomer, %			
		d ₄	d ₃	d ₂	d ₁
2	57.8	100 ^{b, c}	0	0	0
3	10.6	32	8	29	31
4	8.2	100	0	0	0
5	4.2	0	42	43	15
6	12.8	10	83	7	0
7	2.3	0	1	95	4

^a Photolysis conditions: 1-d₄ (0.325 torr) was irradiated with 300 pulses, 0.27 J pulse, with 5 torr SiF₄. T_{max} was 1240 °C.

^b The numbers are the percent of product with the indicated number of deuterium atoms as determined by GC-MS analysis.¹⁶

^c The data are corrected for ¹³C natural abundance and 98.7% deuterium incorporation in 1-d₄.

b) The Reactivity of 1,4-dehydrobenzenes

Investigators: Thomas P. Lockhart and Robert G. Bergman

Important focuses in fossil fuel research include the study of solvents which serve as hydrogen transfer agents in coal liquifaction and the characterization of the reactivity of aromatic radicals which may serve as models for coal "edge" sites. We have examined the reactivity of alkyl substituted 1,4-dehydrobenzenes (aromatic biradicals) with regard to unimolecular and bimolecular hydrogen transfer processes.

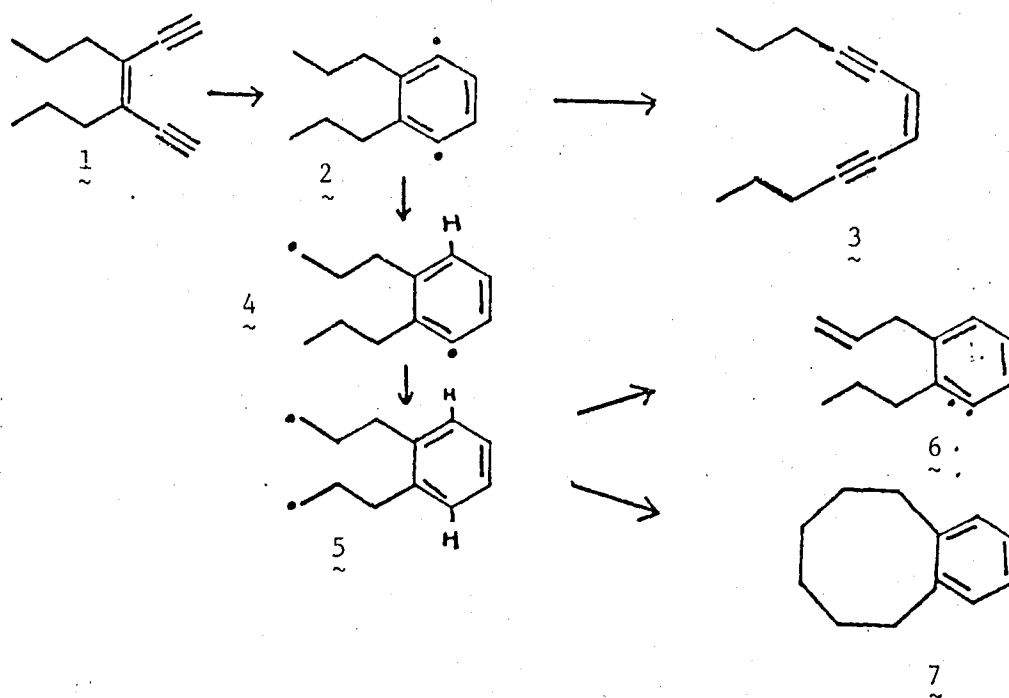
Substituted 1,4-dehydrobenzenes are generated by the thermal reaction of 2,3-dialkyl-hexa-1,5-diyne-3-enes. Our results with octa-4,5-diethynyl-4-ene (1) are summarized in Scheme I. Ring closure produces 2,3-dipropyl-1,4-dehydrobenzene (2) which undergoes several interesting unimolecular reactions. Ring opening to produce isomeric diyne 3, which is stable to the conditions of reaction of 1, occurs in competition with unimolecular [1,5] hydrogen transfer which produces biradical 4. The [1,5] transfer is exothermic by about 12 kcal/mole because a more stable primary alkyl radical is produced. Intramolecular transfer of a second hydrogen atom may take place to produce biradical 5. This biradical may undergo both unimolecular combination and disproportionation reactions, yielding 6 and 7, respectively. When 1 is pyrolyzed in the gas phase a quantitative yield of the three unimolecular products is obtained (Table 1). When pyrolyzed in inert solvent (such as chlorobenzene or diphenyl ether) at 200° C, the same unimolecular products are obtained in good yield.

In the presence of an effective trapping agent such as 1,3-cyclohexadiene, the reduced product (o-di-n-propylbenzene, 8) is obtained in good yield (Table 1). By employing 2,2,5,5-tetradeutero-1,4-cyclohexadiene as trapping agent, 8 containing 2 deuteria/molecule was obtained. By selectively exchanging the aromatic deuteria with protons (by heating with HCl in H₂O) it was possible to determine the position of trapping in 8 (VPC-MS was used to analyze for the relative amounts of d₀, d₁ and d₂ 8 after exchange; these correspond to trapping of trapping of biradical 5, 4, and 3, respectively). The results are summarized in Scheme II, which shows that biradicals 3 and 4 are most efficiently trapped.

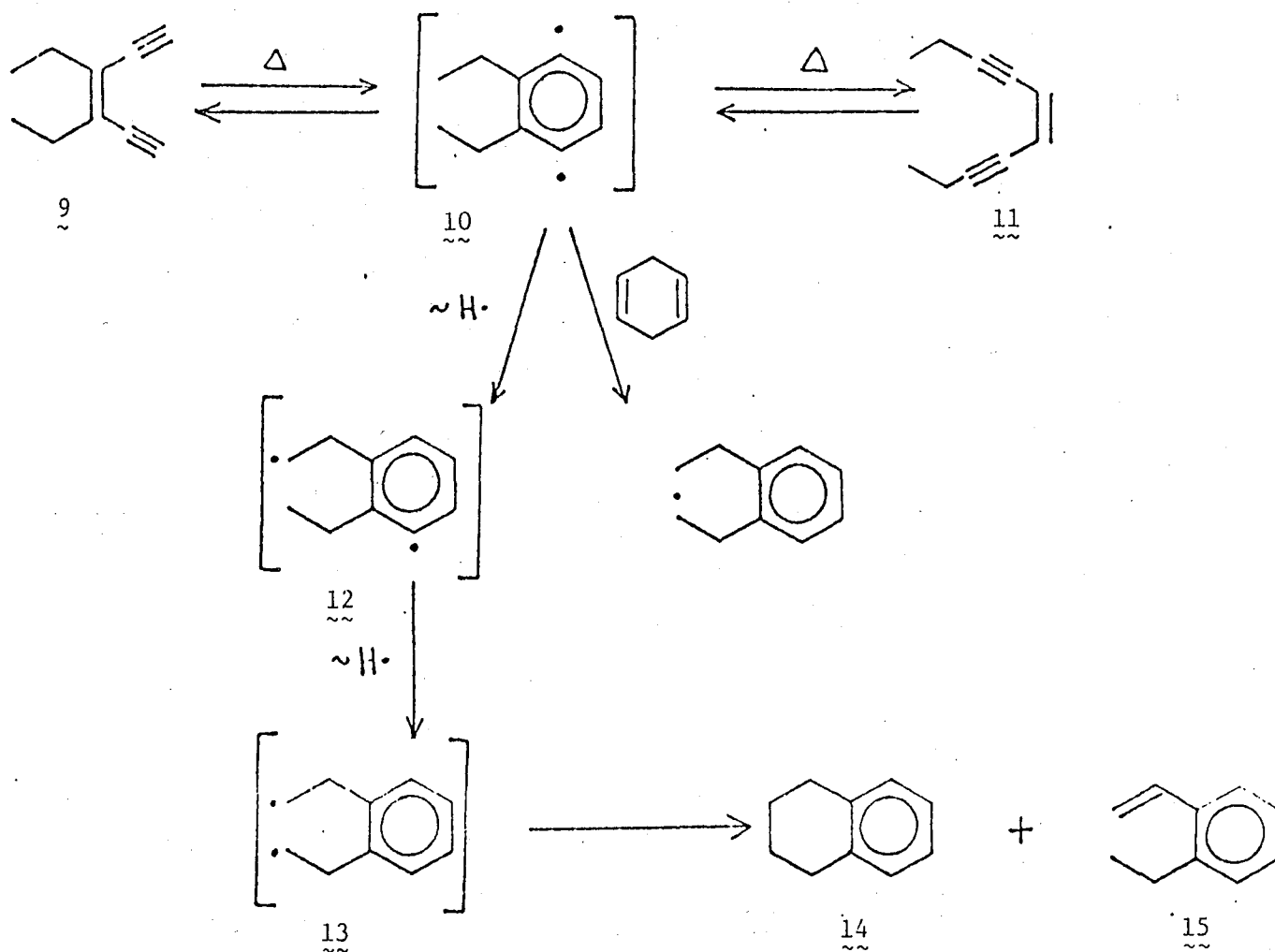
It is interesting to compare the experiments with 1 with those obtained in the pyrolysis of the lower homologue 9. When this compound was heated in the gas phase, formation of the diyne isomer 11 was observed. Only at much higher temperatures (ca. 400° C) do products derived from trapping of the 1,4-dehydroaromatic intermediate (10) appear (Table 2). These products, in particular tetralin (14) and o-ethylstyrene (15),

suggest that [1,4] hydrogen transfer takes place to generate biradicals 12 and 13. When 9 is heated at 190° C in solution (benzene) a high yield of 11 is obtained but products due to intramolecular [1,4] hydrogen abstraction are not observed. When 1,4-cyclohexadiene was added to the reaction solution a good yield of o-diethylbenzene was produced; this is consistent with the formation of biradical 2 as expected in this reaction. These results suggest that [1,4] hydrogen transfer occurs more slowly than either intramolecular ring opening or bimolecular trapping reactions of the biradical 10. The high temperatures required to produce appreciable amounts of intramolecular trapping products in the gas phase suggest that only when 10 is generated repeatedly by the cyclization of 9 and 11 does intramolecular trapping begin to appear. This result stands in contrast to the relative rates of [1,5] hydrogen transfer and ring opening and trapping with 1,4-cyclohexadiene for biradical 2.

In summary, 2,3-dialkyl-1,4-dehydrobenzene biradicals may undergo several different reactions depending on the presence of labile hydrogen atoms in solution and on the position of hydrogen atoms on alkyl side chains. Competitive with fast intermolecular and intramolecular hydrogen abstraction pathways is opening of the aromatic ring to generate diethynyl olefins.



Scheme II



Task 7: Coal Conversion Catalysts - Deactivation Studies

Task Managers: A.V. Levy and E.E. Petersen

Hydrotreating of heavy residual oils and coal-derived liquids is essential for effective utilization of these fuels. However the problem of deactivation of hydrotreating catalysts resulting in reduced catalyst life imposes severe constraints on the technical and economic viability of the upgrading processes. Recent studies⁽¹⁾ of spent cobalt-molybdena-alumina catalysts from hydrotreating units have shown an accumulation of carbon, sulfur and metal compounds and minerals within the pores of the catalyst and as scales on the external surface. This has been reported in detail in an earlier report. (1)

Although the poisoning effects of metals and alkali salts have been recognized for a number of years, very little is known regarding the specific poisoning mechanism and its influence on porosity and diffusion characteristics of the catalyst⁽²⁾. This task is designed to study the scale formation under closely controlled conditions in an effort to understand the causes and mechanism of catalyst deactivation. The porosity and diffusion characteristics of the scale and its influence on product distribution will also be studied. These studies are expected to provide vital information on conditions leading to improved catalyst life and its regeneration techniques.

A laboratory apparatus for preliminary studies of controlled poisoning has been designed and is presently under construction. It is planned to carry out initial deactivation investigations using a batch autoclave reactor equipped with a catalyst basket. Placing the catalyst in the

basket will avoid attrition of the catalyst pellet surface. The major components of the batch unit, are a two-liter autoclave, back pressure regulator, filters and a temperature controller; a sketch of the apparatus is shown in Fig 1. Experimental work utilizing the batch autoclave will commence in the coming quarter. At the same time, a multiphase, continuous, high pressure reactor system for deactivation studies is being designed. The results and conclusions of preliminary studies using the batch reactor will form the basis for the more detailed studies using a continuous laboratory reactor unit.

The feedstock obtained for the deactivation studies are gas oil and the metallic naphthenates of vanadium, nickel, sodium and calcium for the enrichment of the gas oil. The gas oil enriched with metallic naphthenates will be the preferred feedstock due to its low viscosity and ease of maintaining the desired concentration of metals in the feed. It is also planned to enrich gas oil with some of the naturally occurring model organometallic compounds of vanadium, nickel and titanium. The purpose is to learn whether the difference in dominant metals present in synthetic and petroleum liquids leads to different mechanisms of catalyst deactivation. The operating variables for the batch reactor studies will be temperature, pressure, and feed and catalyst compositions. The samples of the catalyst and liquid product will be withdrawn from the reactor and analyzed at regular intervals.

One of the objectives of this investigation is to identify and develop improved deactivation resistant catalysts for hydrotreating of coal-derived liquids. The improvements in composition and structure will be based upon the mechanisms of deactivation determined in the project. The existing hydrotreating catalysts were developed for petroleum

feedstocks and may not be most efficient for coal-derived liquids. The hydrotreating catalysts used during the initial phases of the work will be obtained from various commercial vendors. Samples of the commercial catalysts HDS-16A ($\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$) and HDS-9A ($\text{NiO-MoO}_3/\text{Al}_2\text{O}_3$) manufactured by American Cyanamid Company have been obtained and will be used in the initial experiments. Recently marketed catalysts from the American Cyanamid Company viz. HDS-20, HDS-35 and HDN-30 are on order.

The deactivation mechanisms of commercial catalysts that will be determined are planned to lead to further studies using laboratory-made catalysts with varying surface area and pore-size distribution in an effort to develop a catalyst with improved catalyst life.

The identification and evaluation of various analytical techniques used to determine the degree of deactivation of the catalyst and demetalation of liquid product is also underway⁽³⁾. The samples of fresh and spent catalysts will be characterized using the following techniques: BET surface areas method, mercury porosimetry, X-ray diffraction, electron microscopy (scanning and energy dispersive), electron microprobe, and atomic absorption. The liquid product will be analyzed for sulfur, metals, and carbon-hydrogen.

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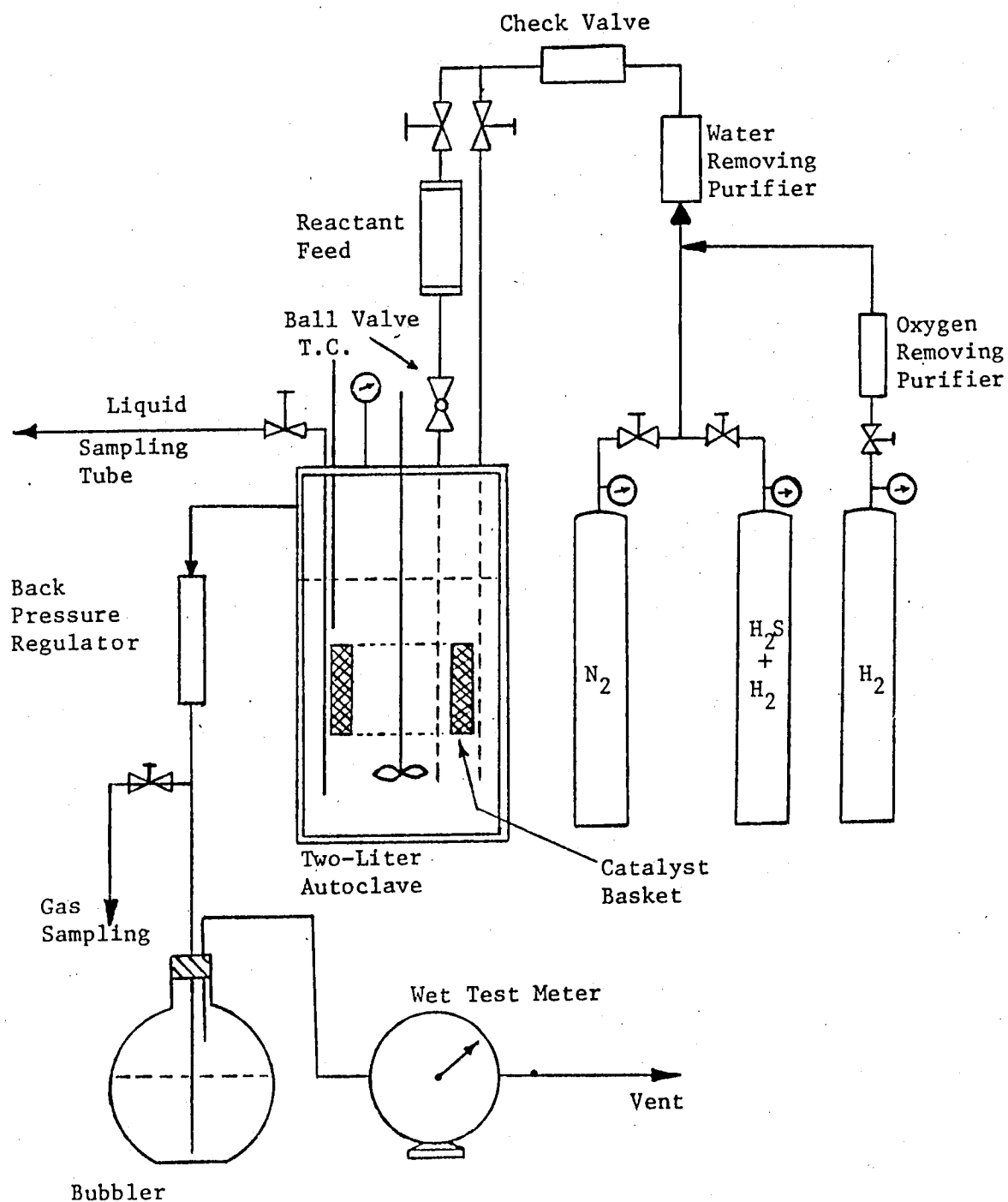


Fig. 1. Schematic Diagram of Catalyst Test System for Batch Hydrotreating Study.